ABSORPTION REVEALS AND HYDROGEN ADDITION EXPLAINS NEW INTERSTELLAR ALDEHYDES: PROPENAL AND PROPANAL

J. M. Hollis[1], P.R. Jewell[2], F.J. Lovas[3], A. Remijan[1,4] and H. Møllendal[5]

ABSTRACT

New interstellar molecules propenal (CH_2CHCHO) and propanal (CH_3CH_2CHO) have been detected largely in absorption toward the star-forming region Sagittarius B2(N) by means of rotational transitions observed with the 100-m Green Bank Telescope (GBT) operating in the range of 18 GHz ($\lambda{\sim}1.7$ cm) to 26 GHz ($\lambda{\sim}1.2$ cm). The GBT was also used to observe the previously reported interstellar aldehyde propynal (HC_2CHO) in Sagittarius B2(N) which is known for large molecules believed to form on interstellar grains. The presence of these three interstellar aldehydes toward Sagittarius B2(N) strongly suggests that simple hydrogen addition on interstellar grains accounts for successively larger molecular species: from propynal to propenal and from propenal to propanal. Energy sources within Sagittarius B2(N) likely permit the hydrogen addition reactions on grain surfaces to proceed. This work demonstrates that successive hydrogen addition is probably an important chemistry route in the formation of a number of complex interstellar molecules. We also searched for but did not detect the three-carbon sugar glyceraldehyde ($CH_2OHCHOHCHO$).

Subject headings: ISM: abundances - ISM: clouds - ISM: individual (Sagittarius B2(N-LMH)) - ISM: molecules - radio lines: ISM

[1]NASA Goddard Space Flight Center, Space and Earth Data Computing Division, Code 930, Greenbelt, MD 20771

[2]National Radio Astronomy Observatory, P. O. Box 2, Green Bank, WV 24944-0002

[3]Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

[4]National Research Council Resident Research Associate

[5]Department of Chemistry, University of Oslo, PO Box 1033, Blindern, N-0315 Oslo, Norway

1. INTRODUCTION

Large molecules found to date in interstellar clouds suggest a grain chemistry that favors aldehyde production. Consistent with this, we (Hollis et al. 2000) successfully detected interstellar glycolaldehyde (CH_2OHCHO) and suggested that it might result from polymerization of two formaldehyde molecules (H_2CO) analogous to the early stage of the sugar synthesis (formose) reaction studied in the laboratory by investigators of prebiotic chemistry. Additionally, laboratory experiments have shown that subjecting cometary ice analogs to ionizing radiation at $\sim$15 K results in solid-phase hydrogen addition reactions (Moore & Hudson 1998). The combination of the prevalence of interstellar aldehydes and the likelihood of subsequent hydrogen addition reactions with aldehydes prompted a successful search for interstellar ethylene glycol ($HOCH_2CH_2OH$) by Hollis et al. (2002). The detection of interstellar ethylene glycol, which differs in constituent atoms of glycolaldehyde by two hydrogen atoms, suggested that ethylene glycol is the product of two successive low-temperature hydrogen addition reactions with glycolaldehyde on grain surfaces or in grain ice mantles. As a consequence of these successes, we were motivated to search for the more complex sugar glyceraldehyde ($CH_2OHCHOHCHO$), which may result from the polymerization of three formaldehyde molecules. Additionally, we searched for simpler aldehydes, specifically propenal (CH_2CHCHO) and propanal (CH_3CH_2CHO) which could be the result of simple hydrogen addition reactions with the known interstellar aldehyde propynal (HC_2CHO) (Irvine et al. 1988; Turner 1991).

2. OBSERVATIONS AND RESULTS

Observations of propynal, propenal, propanal and attempts to detect glyceraldehyde were made in 2004 Feb 25 - Apr 17 with the NRAO[6] 100-m Robert C. Byrd Green Bank Telescope (GBT). Table 1 lists the rotational transitions of the molecules sought. The transition quantum numbers, the transition type, the calculated transition rest frequency, the energy of the lower level (E_l), and the transition line strength (S) are listed in the first five columns. The GBT K-band receiver is divided into two frequency ranges with separate feed/amplifier sets covering 18 - 22.4 GHz and 22 - 26.5 GHz. The GBT spectrometer was configured in its 8 IF, 200 MHz, 3-level mode which allows observing four 200 MHz frequency bands at a time in two polarizations through the use of offset oscillators in the IF. This mode affords 24.4 kHz channel separation. Antenna temperatures are on the T_A^*

---

scale (Ulich & Haas 1976) with estimated 20% uncertainties. GBT half-power beamwidths can be approximated by $\theta_B = 720/\nu(\text{GHz})$ arcseconds. Observations ranged from 18 GHz to 26 GHz which correspond to $\theta_B \sim 40''$ and $\theta_B \sim 28''$, respectively. The SgrB2(N-LMH) J2000 pointing position employed was $\alpha = 17^h47^m19^s.8$, $\delta = -28°22'17''$ and an LSR source velocity (v_{LSR}) of +64 km s^{-1} was assumed. Data were taken in the OFF-ON position-switching mode, with the OFF position 60' east in azimuth with respect to the ON source position. A single scan consisted of two minutes in the OFF source position followed by two minutes in the ON source position. Automatically updated dynamic pointing and focusing corrections were employed based on realtime temperature measurements of the structure input to a thermal model of the GBT; zero points were adusted typically every two hours or less using the calibrators 1626-298 and/or 1733-130. The two polarization outputs from the spectrometer were averaged in the final data reduction process to improve the signal-to-noise ratio.

Observations of propynal, propenal, and propanal are summarized in Table (1) where columns (6), (7) and (8) give measured intensities at LSR velocities of +82, +74, +64 km s^{-1}, respectively; in the case of glyceraldehyde, where no lines were detected, 5 σ noise limits on the spectra are given. Spectra are shown in Figure 1 for propynal, Figure 2 for propenal, and Figure 3 for propanal. In these figures, the absorption components seen have LSR velocities of +64 km s^{-1} and/or +82 km s^{-1} while any emission component seen is centered near +74 km s^{-1}. Moreover, the figures also show that line to continuum ratios of the absorption features associated with propynal, propenal, and propanal indicate apparent optical depths $\ll 1$. Table 1 and the figures show that the lowest energy level transitions observed for each molecule tend to result in emission (e.g. the 2_{02}-1_{01} of propynal and the 1_{11}-0_{00} of propanal) or, at least, some emission (the 2_{11}-1_{10} of propenal). Higher energy level transitions tend toward absorption. This suggests a very low temperature regime (a few K) where the low energy levels are more populated, giving rise to the case where emission dominates the competing effects of absorption. This complication, the likely variance in excitation temperatures among transitions, and the fact that the distribution function over all energy levels is not known, preclude reliable number density estimates.

Other molecular probes toward SgrB2(N-LMH) show that the LSR velocities seen here in propynal, propenal, and propanal are typical and that aldehydes in particular are widespread and would fill the GBT beam. For example, a recent GMRT image and spectrum of the 1_{10}-1_{11} transition of acetaldehyde (CH_3CHO) at 1065 MHz show emission on a scale of at least an arcminute toward SgrB2(N-LMH); that emission is characterized by two LSR velocity components near +64 km s^{-1} and +82 km s^{-1} (see Fig. 1 of Chengalur & Kanekar 2003). Moreover, the spatial scale of glycolaldehyde emission has been shown to be on the order of an arcminute (Hollis et al. 2001) and its LSR velocity is on the order of +72 km s^{-1}

(Hollis et al. 2002). While most large molecules seen in emission toward the hot core source SgrB2(N-LMH) have characteristic LSR velocities near +64 km s^{-1}, recent VLA velocity images of the hot core source molecule ethyl cyanide (CH_3CH_2CN) also show another source $\sim$5″ north of the hot core with a characteristic LSR velocity of +72 km s^{-1} (see Fig. 1 of Hollis et al. 2003); unfortunately, the VLA data did not extend far enough in velocity space to image a potential +82 km s^{-1} source.

The observational evidence for interstellar propanal consists of the six transitions shown in Figure 3 and its identification is secure. By comparison, propenal has only three likely transitions in the 18 - 26 GHz range accessible to the GBT. We have observed two but the third one (2_{02}-1_{01}) is unfortunately frequency coincident with H102γ. However, the observational evidence for propenal is most likely sufficient due to the following arguments: (1) Line confusion is less likely in the K-band range since most molecular transitions of interstellar molecules have peak emission in the mm-wave region of the spectrum due to typical dense cloud temperatures of 50 - 100 K. (2) The two propenal lines as well as the propanal lines are largely in absorption, indicating that the GBT is sampling the much colder, extended, and rarefied foreground gas in the vicinity of SgrB2(N-LMH). (3) Since successive hydrogen addition is the simplest formation mechanism that could account for propenal, then the two lines that we attribute to propenal are securely identified because both the parent molecule, propynal, and the daughter molecule, propanal, are securely identified as interstellar molecules in the same source. We note that Dickens et al. (2001) previously reported the possible detection of propenal at mm-wavelengths, but the group now feels that the assignment is unlikely because the more likely a-type transitions they attempted to observe (e.g. the 10_{09}-9_{09} and the $11_{0,11}$-$10_{0,10}$) were missing (Irvine 2004, private communication).

3. DISCUSSION

Most complex molecules seen in the direction of SgrB2(N-LMH) are shown by interferometry to be largely confined to the Large Molecule Heimat (LMH) region which is a hot core source of $\sim$5″ diameter; such molecules include methyl formate, acetic acid, ethyl cyanide, acetone, formic acid, vinyl cyanide and methyl cyanide. However, the ease with which aldehydes (e.g., formaldehyde, formamide, acetaldehyde, glycolaldehyde, propynal, propenal, and propanal) are detected with single dish telescopes or large synthesized beam interferometers indicate these molecules have significant spatial scales on the order of arc minutes. Since SgrB2 is known for the presence of large-scale shocks (see Chengalar & Kanekar 2003 and references therein), it is likely that the energy source necessary for endothermic reactions to occur on the surfaces or within the mantles of grains are provided by such shocks which

could also account for the release into the gas phase and the widespread distribution of the more common molecules whose formation is aided by this process. Certainly one of the simplest processes in building larger molecular species is successive hydrogen addition to extant grain surface or grain mantle molecules and this is borne out by laboratory experiments with cometary ice analogs (e.g. Moore and Hudson 1998). The detection of interstellar propynal, propenal, and propanal in the same source strongly implies the following hydrogen addition formation sequence:

$$HC_2CHO + 2H \rightarrow CH_2CHCHO + 2H \rightarrow CH_3CH_2CHO$$

Aldehydes have been called the 'sugars of space' ever since the discovery of interstellar formaldehyde by Snyder et al. (1969). This title took on greater significance with the detection of the simplest sugar glycolaldehyde (Hollis et al. 2000). These authors suggested that formaldehyde polymerization on interstellar grains may be responsible to the formation of glycolaldehyde and more complex sugars – an interstellar variant of the so-called formose reaction which has been extensively studied in the laboratory with regard to prebiotic chemistry (Larralde, Robertson, & Miller 1995). In the initial stages of the formaldehyde polymerization, glycolaldehyde is produced and rapidly thereafter glyceraldehyde, the next more complex sugar (see Walker 1975). Our difficulty in attempting to detect glyceraldehyde (see Table 1 limits) suggests that, if interstellar glyceraldehyde exists, it is much more spatially extended such that our telescope beam does not subtend a large enough column of material adequate for detection or, alternatively, a slower, less efficient process than the formose reaction produces it. Based on our simpler aldehyde observations that are most easily explained by hydrogen addition, we suggest that cometary ice analog experiments with glycolaldehyde that facilitate carbon, oxygen, and hydrogen addition reactions may eventually be able to produce glyceraldehyde.

In summary, we have detected two new interstellar molecules propenal and propanal largely in absorption toward the star forming region of SgrB2(N). We also found propynal, a previously reported molecule, in the same region. These findings strongly indicate that two successive hydrogen additions on interstellar grains produce propenal from propynal; similarly, two successive hydrogen additions produce propanal from propenal. This result is supported by laboratory experiments that indicate low-temperature solid-phase hydrogen additions are responsible for the production of more complex molecules from simpler species. We searched for the 3-carbon sugar glyceraldehyde and were not successful. As a result, we conclude that an efficient formaldehyde polymerization chemistry is not the likely production mechanism for either glycolaldehyde or glyceraldehyde.

REFERENCES

Blom, C.E., Grassi, G., & Bauder, A. 1984, J. Am. Chem. Soc., 106, 7427

Brown, R.D., & Godfrey, P.D. 1984, Aust. J. Chem., 37, 1951

Butcher, S.S., & Wilson, E.B., Jr. 1964, J. Chem. Phys., 40, 1671

Chengalur, J.N., & Kanekar, N. 2003, A&A, 403, L43

Dickens, J.E., Irvine, W.M., Nummelin, A., Møllendal, H., Saito, S., Thorwirth, S., Hjalmarson, Å., & Ohishi, M. 2001, Spectrochim. Acta, 57, 643

Hollis, J.M., Lovas, F.J., & Jewell, P.R. 2000, ApJ, 540, L107

Hollis, J.M., Lovas, F.J., Jewell, P.R., & Coudert, L.H. 2002, ApJ, 571, L59

Hollis, J.M., Pedelty, J.A., Boboltz, D.A., Liu, S.-Y., Snyder, L.E., Palmer, P., Lovas, F.J., & Jewell, P.R. 2003, ApJ, 596, L235

Hollis, J.M., Vogel, S.N., Snyder, L.E., Jewell, P.R., & Lovas, F.J. 2001, ApJ, 554, L81

Irvine, W.M., Brown, R.D., Cragg, D.M., Friberg, P., Godfrey, P.D., Kaifu, N., Matthews, H.E., Ohishi, M., Suzuki, H., & Takeo, H. 1988, ApJ, 335, L89

Langston, G. 2004, AJ, (in prep)

Larralde, R., Robertson, M.P., & Miller, S. 1995, Proc. Natl. Acad. Sci., 92, 8158

Lovas, F.J., Suenram, R.D., Plusquellic, D.F., & Møllendal, H. 2003, J.Mol.Spect., 222, 263.

Moore, M.H., & Hudson, R.L. 1998, Icarus, 135, 518

Snyder, L.E., Buhl, D., Zuckerman, B., & Palmer, P. 1969, Phys. Rev., 22, 679

Taylor, B.N., & Kuyatt, C.E. 1994, NIST Tech. Note 1297, US Govt. Printing Office, Washington D.C.

Turner, B.E. 1991, ApJS, 76, 617

Ulich, B.L., & Haas, R.W. 1976, ApJS, 30, 247

Walker, J.F. 1975, Formaldehyde (3d ed.; Huntington: Robert E. Krieger), p. 217

Table 1.   Summary of Spectral Line Observations Toward
SgrB2(N-LMH)

Transition J'_{K-K+}-J''_{K-K+} (1)	Type (2)	Frequency (MHz) (3)[a]	E_l (cm^{-1}) (4)	S (5)	+82 (6)[b]	+74 ΔT^*_A (mK) (7)[b]	+64 (8)[b]
Propynal (HC_2CHO)[c]							
2_{02}-1_{01}	a-type	18650.308(4)	0.31	2.000	-3(1)	11(1)	-14(1)
Propenal (CH_2CHCHO)[d]							
2_{11}-1_{10}	a-type	18221.164(2)	1.74	1.500	-29(2)	14(2)	...
3_{13}-2_{12}	a-type	26079.449(1)	2.30	2.667	-9(1)	...	-19(1)
Propanal (CH_3CH_2CHO)[e,f]							
1_{11}-0_{00}	b-type	21268.611(9)	0.00	1.000	...	6(1)	...
2_{02}-1_{01}	a-type	20875.059(7)	0.35	1.995	...	5(1)	-7(1)
2_{12}-1_{11}	a-type	19690.426(7)	0.71	1.500	-4(1)	...	-18(1)
2_{11}-1_{10}	a-type	22279.346(7)	0.75	1.500	...	...	-8(1)
3_{03}-2_{12}	b-type	21451.572(8)	1.37	1.284	-3(1)	...	-16(1)
4_{13}-4_{04}	b-type	19182.445(10)	3.45	3.383	-5(1)	6(1)	-9(1)
Glyceraldehyde ($CH_2OHCHOHCHO$)[g]							
2_{21}-1_{11}	c-type	19193.051(2)	0.26	1.500		<5	
2_{20}-1_{10}	c-type	18845.484(2)	0.28	1.597		<5	
3_{12}-2_{02}	c-type	19623.303(2)	0.52	1.934		<5	
4_{13}-3_{03}	c-type	25656.520(1)	1.03	2.254		<10	
6_{51}-6_{43}	c-type	25724.488(3)	5.18	1.560		<10	
7_{53}-7_{43}	c-type	25655.113(3)	6.40	2.181		<10	
8_{53}-8_{45}	c-type	25612.418(3)	7.79	2.732		<15	
13_{56}-$13_{4,10}$	c-type	25618.963(8)	17.40	4.550		<10	

[a]Uncertainties in parentheses refer to the least significant digit and are 2 σ values (Taylor & Kuyatt 1994).

[b]Uncertainties are 1 σ values and limits are 5 σ.

[c]Propynal: μ_a = 2.359(18) D and μ_b = 1.468(22) D (Brown & Godfrey 1984)

[d]Propenal: μ_a = 3.052(4) D and μ_b = 0.630(1) D (Blom, Grassi, & Bauder 1984)

[e]Propanal: μ_a = 1.71(4) D and μ_b = 1.85(4) D (Butcher & Wilson 1964)

[f]The E-State is approximately frequency coincident and can not be resolved in a dense cloud.

[g]Glyceraldehyde: μ_a = 0.459(3) D and μ_b = 0.36(4) D and μ_c = 2.068(8) D (Lovas et al. 2003)

Fig. 1.— Propynal (HC$_2$CHO) spectrum toward SgrB2(N-LMH) at 24.4 kHz channel spacing. Transition quantum numbers are shown in the upper right. The spectrum was processed with a median filter to remove instrumental slopes in the bandpass (Langston 2004). The abscissa is the radial velocity with respect to the LSR calculated for the rest frequency of the transition shown (see Table 1) at an assumed source velocity of 74 km s^{-1}. Dashed lines show LSR velocities at 64, 74 and 82 km s^{-1}. The continuum level of the source is shown as a component of the temperature scale.

Fig. 2.— Propenal (CH$_2$CHCHO) spectra toward SgrB2(N-LMH) at 24.4 kHz channel spacing. Figure 1 caption applies. Panel a) is the low energy level transition and panel b) is the higher energy level transition observed (see Table 1).

Fig. 3.— Propanal (CH$_3$CH$_2$CHO) spectra toward SgrB2(N-LMH) at 24.4 kHz channel spacing. Figure 1 caption applies. Panels a) through f) are ordered from the lowest energy level transition to the highest energy level transition observed (see Table 1).
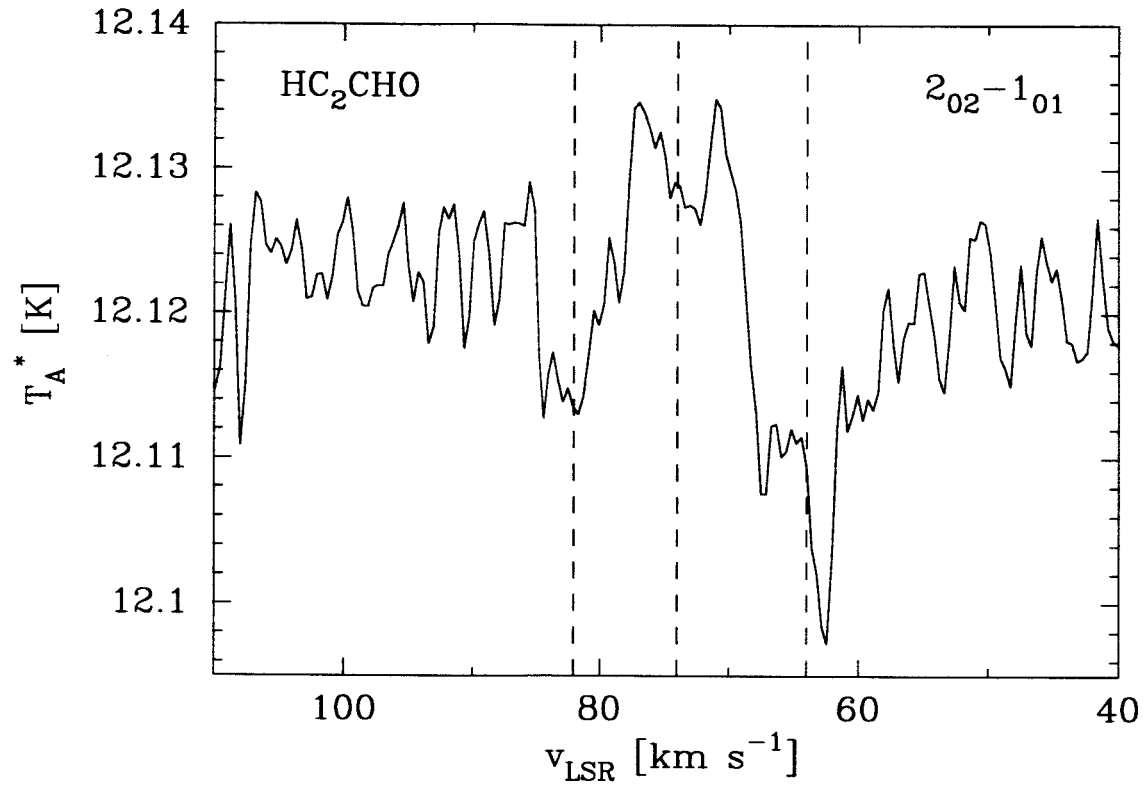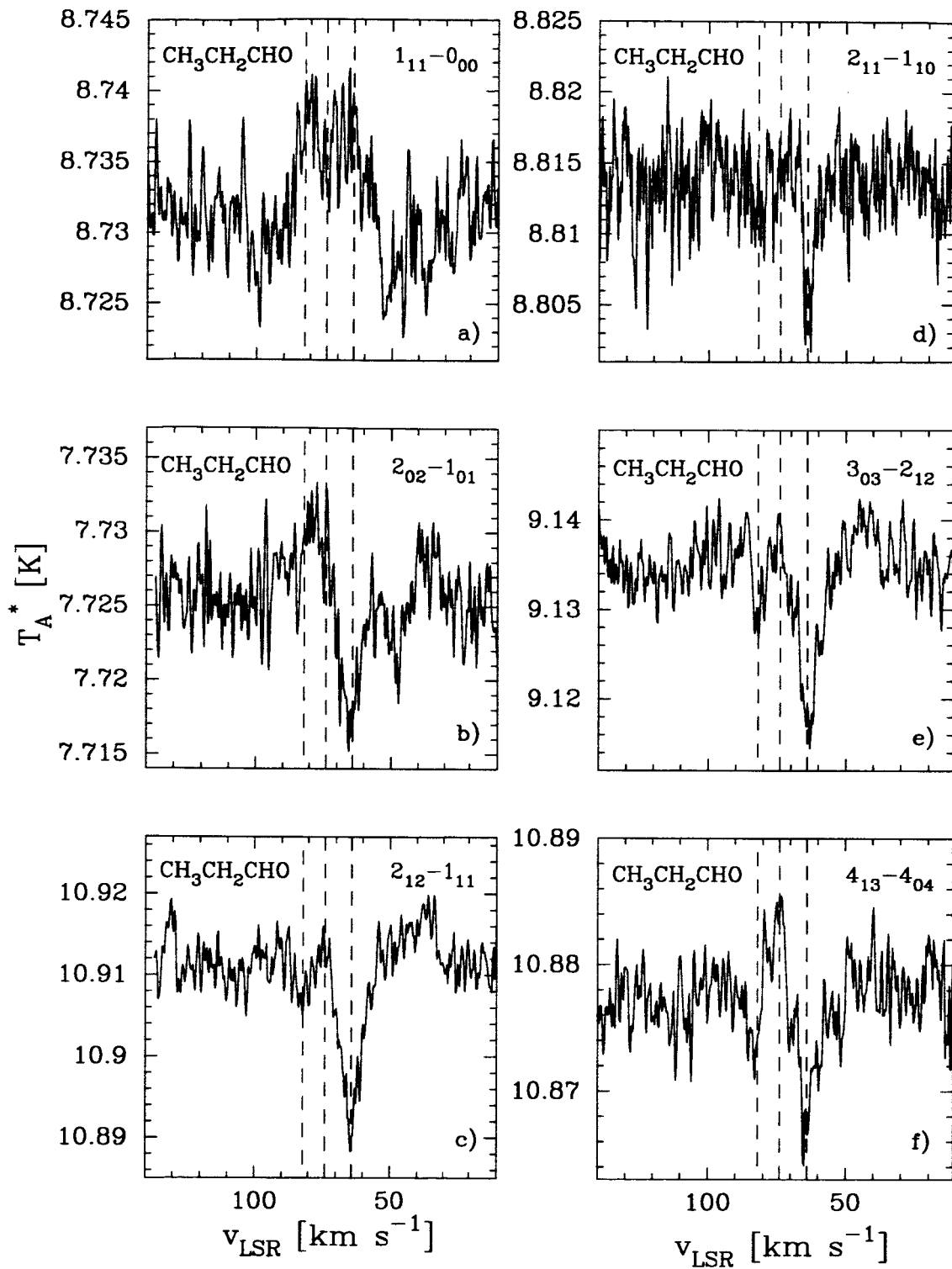
Figure 1.

Figure 3.